USE OF CALCIUM SULFITE -- CONTAINING FLUE GAS DESULFURIZATION (FGD) BY -- PRODUCT TO INHIBIT ACID MINE DRAINAGE FROM COAL REFUSE

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Abstract

Calcium sulfite ($CaSO_3$) contained in flue gas desulfurization (FGD) by -- product is a strong reductant, an alkaline material, and a toxicant against pyrite -- oxidizing bacteria. These chemical properties of $CaSO_3$ are all useful in inhibiting formation of acid in coal refuse. In a lab -- scale column (2.5 x 13 cm) leaching experiment, 10 g FGD containing 6.4 g $CaSO_3$, 1 g $CaCO_3$, 0.9 g $CaSO_4$, and 1.7 g fly ash were applied to 50 g ground (<2 mm) fresh coal refuse. Calcium sulfite, $CaCO_3$, and fly ash were also applied individually and in combination to the coal refuse. During 27 weeks of leaching with water, $CaSO_3$ inhibited the onset of acid production in coal refuse. Such inhibition was enhanced by $CaCO_3$ and fly ash and these materials in combination with $CaSO_3$ resulted in the FGD having the strongest inhibitory effect. In a greenhouse column (30 x 112 cm) leaching experiment, the FGD was incorporated into fresh coarse coal refuse at 5.5%, 11%, and 22% (w/w) in the surface (0 -- 15 cm) layer, and FGD was applied at a rate of 1.25%, 2.5%, and 5.0% (w/w) in the middle (50 -- 65 cm) layer. The low rate of FGD in the surface layer was matched with the low rate in the middle layer and this experimental design was also used for the other two rates. During 39 weeks of leaching, all FGD treatments significantly decreased leachate acidity and increased leachate pH. This effect increased with increasing FGD rates. We conclude that application of $CaSO_3$ -- based FGD to coal refuse is a potential new method to inhibit acid mine drainage and field test needs to be conducted.

Introduction

Pyrite oxidation in coal mine spoil and coal wastes produces copious amounts of acid based on the following reactions (Nordstrom and Southam, 1997):

$$2FeS_2 + 7.5O_2 + H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{2-}$$

Acid drainage can create severe environmental degradation. Various methods have been developed to abate acid drainage by removal of the reactants such as oxygen, ferric ion, and water, by neutralization of hydrogen ion, and by inhibition of sulfur -- and iron -- oxidizing bacterial activity.

To limit the contact of pyrite with oxygen and/or water cementitious materials created by mixing fly ash and portland cement (Gabr et al., 1994), plastic liners (Meek, 1994), and soil caps (Bell et al., 1994) have been used to create a physical barrier. Stimulation of vegetative cover using organic compost (Hoitink and Watson, 1982; Pichtel et al., 1994; Sopper, 1992) and sewage sludge (Sopper, 1992) have also been used to reduce pyrite exposure to oxygen. Various alkaline materials can neutralize hydrogen ion and limit ferric ion activity in water. These materials include limestone (Pietz et al., 1989a, b, c), alkaline fly ash (Sutton and Dick, 1987), FGD (Dick et al., 1994; Stehouwer et al., 1995a, b, c and 1998), steel making slags (Skousen and Ziemkiewicz, 1995), phosphate (Evangelou, 1995), and organic acids (Pichtel and Dick, 1991; Pichtel et al., 1989). Bactericides such as lauryl sulfate and sodium benzoate may be used to inhibit sulfur -- and iron -- oxidizing bacterial activity (Kelley and Tuovinen, 1988; Rastogi, 1996).

The above methods have attained some success in inhibiting acid formation. However, none of the above methods can exert the following multiple inhibitory effects on pyrite oxidation which are removal of oxygen and ferric ion, neutralization of acid, and inhibition of sulfur -- and iron -- oxidizing bacterial activity. Calcium sulfite meets all of these criteria because of its chemical properties. It is also readily availability because it is formed in large amounts by coal burning utilities as a by-product of the SO_2 scrubbing reaction. Each year large quantities of $CaSO_3$ are disposed of in landfills, but if mixed with coal refuse at the time the refuse is disposed, it could actually provide a benefit by inhibiting acid formation.

Sulfite salts (sodium and potassium) which are highly soluble in water have been used as antioxidants in the food and drug industry for many years (Schroeter, 1963). In contrast, $CaSO_3$ has a low solubility in water. In the past several years, we have tested the efficiency of $CaSO_3$ in scavenging oxygen and ferric ion out of water. The results showed $CaSO_3$ can rapidly react with oxygen and ferric ion under different pHs, temperatures, and oxygen partial pressures, the conditions which can be encountered in coal refuse disposal environments (Hao, 1998). In the presence of $CaSO_3$, dissolved oxygen concentration in water was below 10 ppb (Hao, 1998). This highly anaerobic condition created by $CaSO_3$ would be effective in suppressing abiotic and biotic oxidation of pyrite. Studies conducted by other researchers also indicate sulfite is toxic to sulfur -- and iron -- oxidizing bacteria due to formation of chemical radicals during sulfite oxidation (Hurtado et al., 1987; Ough, 1993; Sugio et al., 1994).

Because of the potential multiple inhibitory effects of $CaSO_3$ on pyrite oxidation, we conducted column leaching experiments to determine: (1) the inhibitory effect of $CaSO_3$ on acid leaching from coal refuse; (2) the interaction of $CaSO_3$ with the other two major FGD components, i.e. $CaCO_3$ and fly ash, in inhibiting acid production in coal refuse; and (3) the inhibitory effect of $CaSO_3$ -- based FGD on acid leaching.

Materials and Methods

Fresh (unweathered) coal refuse, FGD, and fly ash were obtained from the American Electric Power Plant (Coshocton, Ohio). The coal refuse was coarse (36% of the particles had sizes of 1 -- 10 mm in diameter and 64% were greater than 10 mm in diameter) and was produced by a gravity separation method. X -- ray diffraction analysis (Stehouwer et al., 1995a) indicated that the coal refuse contained gypsum, kaolinite, marcasite, pyrite, and quartz. The fly ash was collected in an electrostatic precipitator. The FGD by -- product was produced in the power plant by mixing filter cake ($CaSO_3$), fly ash, and lime and was weathered for several weeks on the landfill site near the power plant. Particle sizes of the FGD were less than 0.5 mm. Thermogravimetric analysis (Stehouwer et al., 1995a) indicated that the FGD contained 64% $CaSO_3$, 10% $CaCO_3$, 9% gypsum ($CaSO_4 \, 2H_2O$), and 17% fly ash. Calcium sulfite (96% purity) was synthesized in our lab and was ascertained to be hannebachite by X -- ray diffraction analysis (Hao, 1998). Calcium carbonate was a reagent grade chemical.

Total element concentrations (Table 1) in the above materials were analyzed by an aqua regia -- HF digestion and inductively -- coupled plasma (ICP) emission spectroscopy (Hao, 1998). Total neutralization potential (TNP) was determined by the following procedure: samples were oxidized with 30% H_2O_2 for 30 min, acidified with 0.2 M HCl, heated for 30 min and then cooled before back -- titrating with 0.5 M NaOH to pH 7.0.

Table 1. Chemical composition of the coal refuse and amendments used in the column leaching experiments.

Sample	pH	TNP[a]	Element concentrations													
			Al	Ca	Fe	K	Mg	Na	Si	S	As	Mn	Ni	Pb	Se	Zn
							%						mg kg^{-1}			
$CaSO_3$	9.7	3%	0.005	3.1	0.004	0.032	0.002	0.000	0.001	25	63.0	0.00	3.52	0.00	29.2	0.46
Fly ash	3.9	0%	12	1.9	18	1.2	0.52	0.47	19	0.46	201	301	168	561	2960	247
FGD	10.6	11%	5.6	18	6.7	0.50	0.68	0.41	10	7.3	36.0	145	99.2	300	3300	118
Coal refuse	4.2	ND[b]	3.5	0.36	10	0.45	0.21	0.37	9.0	11	230	140	88.1	354	3690	87.0

[a], TNP = total neutralization potential calculated as a percentage of $CaCO_3$ equivalence.

[b], ND = not determined.

Lab -- scale column leaching experiments were conducted using plastic syringes (2.5 x 13 cm). Fifty grams of air -- dried and ground coal refuse (particle size < 2 mm) were thoroughly mixed with different amendments and then placed in the columns. Glass wool was packed in the bottom (1 g) and at the top (0.2 g) of the syringes to facilitate water movement through the columns. Seven treatments were investigated and included: $CaSO_3$, $CaCO_3$, fly ash, combination of $CaSO_3$ with $CaCO_3$, combination of $CaSO_3$ with fly ash, FGD, and an untreated control. The amount of FGD added to coal refuse was 10 g (20% rate, w/w). The amounts of $CaSO_3$ (6.4 g), $CaCO_3$ (1 g), and fly ash (1.7 g) were equal to the amounts contained in 10 g FGD. Each treatment was replicated three times. The experimental design was a randomized complete block. The columns were leached weekly for the first 13 weeks and biweekly for the last 14 weeks (total 27 weeks). For each leaching, 20 ml of double deionized water was added to the columns. The leaching speed was 1 ml per hour and was controlled by a mechanical extractor (Model 24 -- 01, Centurion International Inc., Lincoln, NC).

Greenhouse column leaching experiments were conducted using coal refuse with particle sizes less than 10 cm. The refuse was packed into large PVC columns (30 x 120 cm) in four layers (Fig. 1). The first two layers of refuse were packed into the columns during 25-30 July, 1996 and the other layers were added two weeks later. These packings included a 35 cm layer of untreated coal refuse (30 kg dry weight) topped with an additional 15 to 25 cm layer of the mixture of coal refuse (13 kg dry weight) and FGD. Before mixing with refuse, large chunks of FGD formed in the weathering process were broken by hand and passed through a 1 -- cm sieve. At the bottom of the columns, two glass wool mats separated by a 4 cm layer of quartz pebbles (> 1 cm) were placed to facilitate water movement to the drainage holes (1 cm in diameter, Fig. 1). The temperature in the greenhouse was approximately 25^0 C. There were four FGD treatments and the FGD was incorporated into the top (0 to 15 cm) layer at 0%, 5.5%, 11%, and 22% (w/w). To the lower middle (50 to 65 cm) layer of the same columns additional FGD was applied at 0%, 1.25%, 2.5%, and 5.0%. The low rate of FGD in the surface layer was matched with the low rate in the middle layer and the middle rate and high rates of FGD were also matched in the two treated layers. Each treatment was replicated three times to give a total of 12 columns. The experimental design was a randomized complete block. The paste pH values (1:1, water) of the untreated coal refuse and the columns treated with FGD were, in order from zero to highest rate, 3.81, 7.88, 7.99, and 9.17 for the top layer and 3.29, 5.19, 5.97, 5.60 for the lower middle layer.

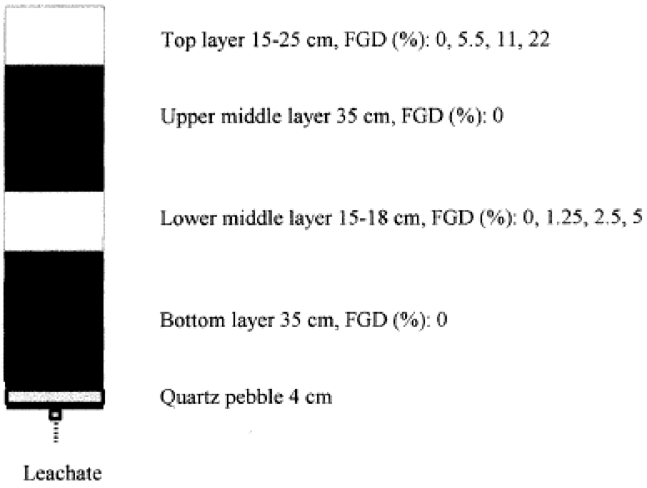

Fig. 1. Structure of greenhouse column (30 x 120 cm) containing four layers of coal refuse for leaching experiment.

The first leaching was initiated one day after the first packing of the coal refuse was completed and is referred to as the week zero leaching. All subsequent leachings were made on the last day of the week and were designated by their week numbers. The columns were leached for three consecutive periods: weekly from weeks 0 to 13, biweekly from weeks 13 to 27, and monthly from weeks 27 to 39. From weeks 0 to 5, the leachings were conducted by adding 1000 to 2500 ml of water over a one to two day period. This amount of water was required to fully moisten the coal refuse and to obtain a sufficient volume of leachate for analysis. From weeks 6 to 39, two, 500 -- ml doses of distilled water (total 1000 ml) were added two hours apart to the top of each column. Gravity flow leachate was collected for 24 h in plastic bottles placed under the columns. The leachate volumes obtained generally ranged from 25 to 500 ml.

Leachates were analyzed for pH (glass electrode), titratable acidity (end point pH 8.3), and concentrations of dissolved (filtrates pass through 0.45 m filter paper) elements including Al, As, B, Ca, Fe, Mg, Mn, Ni, Pb, S, Se, and Zn by ICP. For the lab -- scale column leaching experiment, the total amounts (concentration x 20 ml x number of leachates) of acidity,

H^+, Fe, and Al in leachates were calculated for the weekly (weeks 1 to 13) and biweekly (weeks 13 to 27) leaching periods. The interactions of $CaSO_3$ with $CaCO_3$ and fly ash were analyzed by factorial tests (2 factors x 2 levels). The two factors were $CaSO_3$ and $CaCO_3$ or $CaSO_3$ and fly ash, and the two levels were the control vs treated columns. To compare the effects of different treatments on acid leaching from the coal refuse in greenhouse columns, mean values of acidity, pH, and concentrations of dissolved elements were calculated for the four leaching periods: weekly (weeks 0 to 13), biweekly (weeks 13 to 27), monthly (weeks 27 to 39), and total leaching period (weeks 0 to 39). These mean values were analyzed for the least significance difference (LSD) test, t tests, and linear contrasts using the SAS program (SAS Institute, 1988). Significant differences were based on a confidence level of 95% ($p < 0.05$).

Results and Discussion

The acidities reported in this research are extraodineously high due to the column setup and leaching procedure for rigorous test and thus would not be commonly found in the field.

Lab -- scale column leaching experiment. The coal refuse rapidly produced acid and during the initial 4 weeks, the leachate acidity of the control increased from 8000 to 34000 mg $CaCO_3$ L^{-1} and the leachate pH dropped from 2.61 to 1.12 (Fig. 2). Calcium sulfite inhibited the onset of acid leaching from the coal refuse. During the initial 4 weeks, the leachate acidity of the $CaSO_3$ treatment was below 150 mg $CaCO_3$ L^{-1} and the leachate pH was higher than the initial pH (2.82) (Fig. 2). For the initial 13 weeks, the leachate acidity of the $CaSO_3$ treatment was at least 6500 mg $CaCO_3$ L^{-1} lower than that of the control for each leachate. Concentrations of Fe and Al were also decreased by the $CaSO_3$ treatment (data not shown). The inhibitory effect of $CaSO_3$ on acid leaching from the coal refuse was much less effective during the last 14 weeks than the initial 13 weeks, although the acidities of the last 7 leachates of $CaSO_3$ treatment were always lower than those of the control (Fig. 2).

Flue gas desulfurization by-product (which is a mixture of $CaSO_3$, $CaCO_3$, $CaSO_4$, and fly ash) showed the strongest inhibitory effect on acid leaching from the coal refuse (Fig. 2). The FGD treatment produced leachates with acidity near zero for weeks 2 to 10 and pH reached a maximum of 8.14 during week 6 and remained above 5.35 for the entire initial 13 week period. Because $CaCO_3$ and fly ash showed weak or no inhibitory effects on acid leaching, respectively (Fig. 2), $CaSO_3$ is believed to be a main contributor to the strong inhibitory effect of the FGD on acid leaching. This suggests that $CaCO_3$ and fly ash enhanced the inhibitory effect of $CaSO_3$ on acid leaching through some positive synergistic mechanisms (Fig. 3). The enhancement of the inhibitory effect of $CaSO_3$ on acid leaching by $CaCO_3$ and fly ash is thought to be due, in part, to the dependence of dissolution and oxidation of $CaSO_3$ on pH and oxygen diffusion rate from the atmosphere into coal refuse (Hao, 1998). Calcium carbonate may increase the persistence of $CaSO_3$ in the coal refuse columns by increasing pH and thus decreasing dissolution (leaching) and oxidation of $CaSO_3$. The fine grain size of fly ash may also retard oxygen diffusion from the atmosphere into the coal refuse. The above mechanisms suggests that for utilization of the chemical properties of $CaSO_3$ in inhibition of acid production in coal refuse, it is preferable to apply $CaSO_3$ at depth instead of on the surface of coal refuse and to apply $CaSO_3$ -- based FGD containing $CaCO_3$ and fly ash, instead of applying $CaSO_3$ alone.

Greenhouse column leaching experiment. The FGD treatments significantly decreased leachate acidity and increased leachate pH throughout the entire leaching period compared to the control (Fig. 4). Starting from week 3 (after completing the second addition of coal refuse to the columns), the 22% FGD treatment produced leachate acidity that was 25000 mg $CaCO_3$ L^{-1} lower and a pH at least 0.5 units higher than measured for the control. During the initial 27 weeks, the 22% FGD treatment also significantly reduced the concentrations of various elements such as Al, As, Fe, Ni, Pb, S, and Zn (Table 2). The decrease of leachate acidity and Fe concentration and the increase of leachate pH responded linearly to the increasing FGD rates.

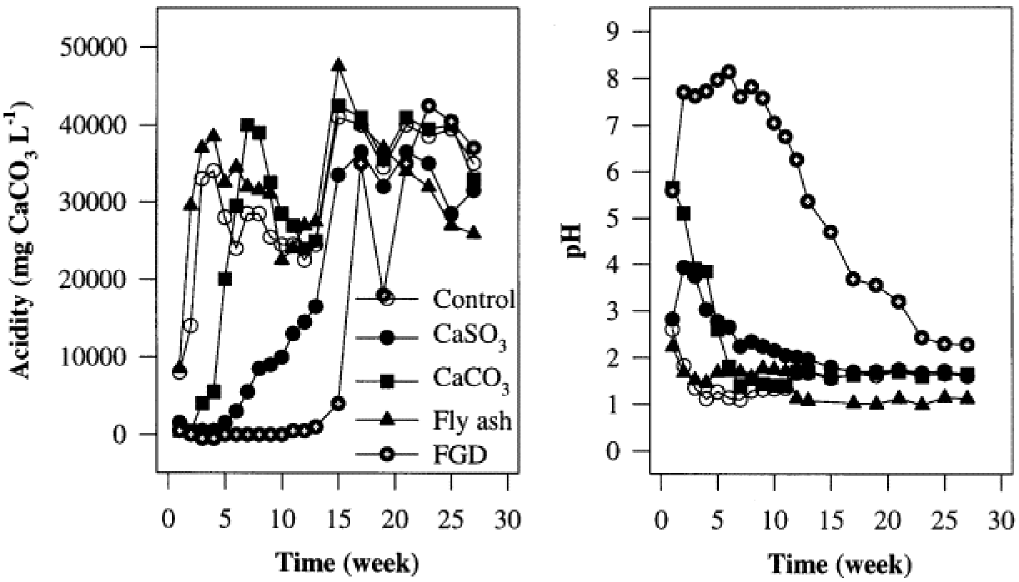

Fig. 2. Change of leachate acidity and pH with time in the lab-scale column (2.5 x 13 cm) leaching experiment. The fresh ground coal refuse was amended with $CaSO_3$, $CaCO_3$, fly ash, and FGD and leached for 27 weeks.

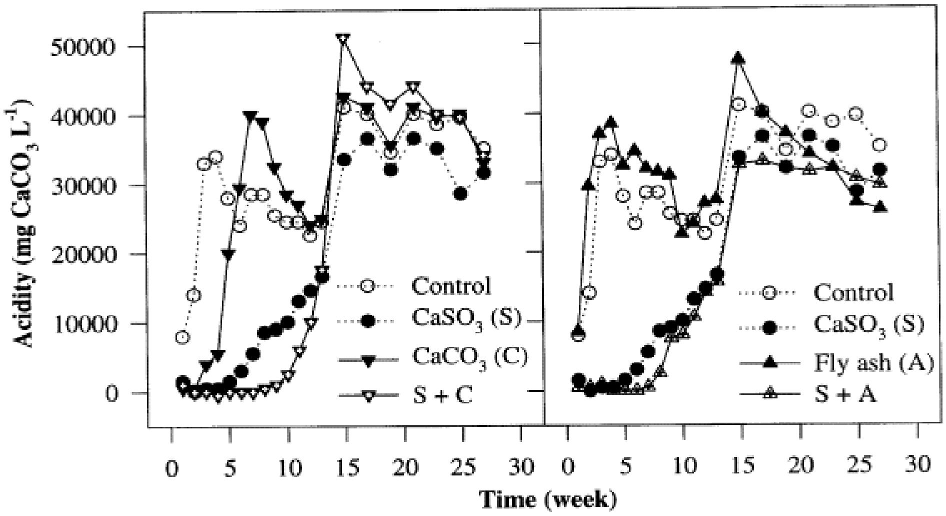

Fig. 3. Effect of combination of $CaSO_3$, with $CaCO_3$ (left plot) or fly ash (right plot) on inhibition of acid production in leachate in the lab-scale column (2.5 x 13 cm) leaching experiment.

Although the leachate acidity increased and the leachate pH decreased with time for all treatments during the initial 27 weeks, the differences in leachate acidity and pH between the control and the FGD treatments (especially the 22% FGD treatment) became larger with time (Fig. 4). Therefore, the inhibitory effect of the FGD treatments on acid leaching from the coal refuse became more obvious with time.

The large column experiments were set up to mimic, as much as possible, conditions in the field. The results obtained are encouraging because they clearly show that FGD can be beneficial in reducing acid formation when mixed with coal refuse. The FGD by-product has several properties that make it desirable for treating coal refuse. Calcium sulfite in the FGD acts as an oxygen scavenger creating a chemical oxygen transport barrier to the refuse. Also, sulfite is toxic to *Thiobacillus* bacteria that oxidizes pyrite. Compacted scrubber sludge has a low hydraulic conductivity and functions as a physical barrier to water transport. Unreacted lime in the scrubber sludge neutralizes acidity and further reduces *Thiobacillus* activity. The combined effect of these FGD properties is the creation of an environment that prevents acid formation and the data support this assessment.

Conclusions

Calcium sulfite can inhibit acid production in coal refuse. Calcium carbonate and fly ash enhances the inhibitory effect of $CaSO_3$. To utilize the chemical properties of $CaSO_3$ for inhibition of acid production in coal refuse, the use of $CaSO_3$ --

based FGD is a better choice than using $CaSO_3$ alone and subsurface application would be more effective than surface application. The inhibitory effect of the $CaSO_3$ -- based FGD on acid leaching from greenhouse coal refuse columns provides strong support for moving this work to the field and for testing the use of $CaSO_3$ -- based FGD for prevention of acid formation under field conditions.

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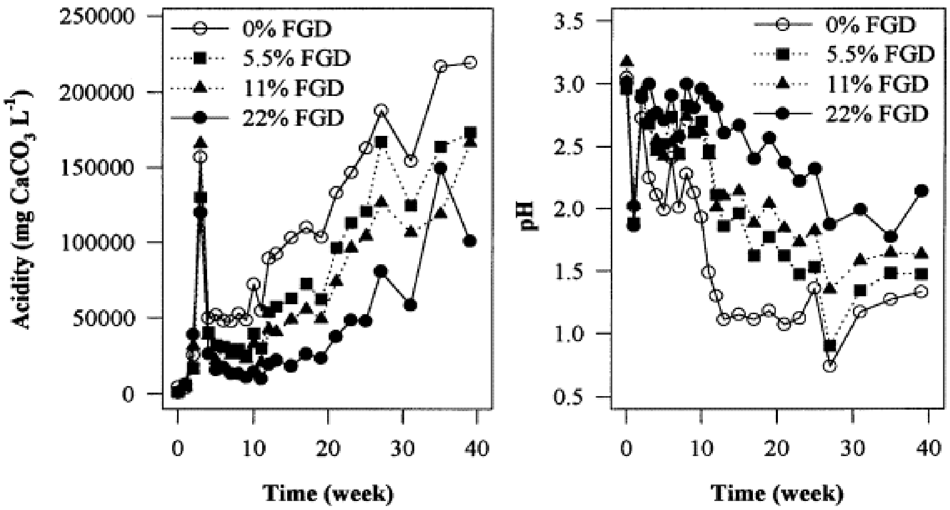

Fig. 4. Change of leachate acidity and pH with time in the greenhouse column (30 x 120 cm) leaching experiment. The fresh coarse coal refuse was amended with various rates of FGD and leached for 39 weeks.

Table 2. Comparison of element concentrations in leachate collected from columns with or without FGD addition.

Time (weeks)	FGD treatment[a]	Element concentrations in leachate (mg L^{-1})											
		Al	As	B	Ca	Fe	Mg	Mn	Ni	Pb	S	Se	Zn
1	0	102	3.12	0.31	484	1710	723	32.7	5.10	0.08	2680	2.01	9.32
	22	149	1.94	0.88	494	2460	765	36.4	6.61	0.52	3360	9.51	11.5
2	0	511	3.21	<0.01	528	10600	1660	88.5	18.2	0.77	10100	0.30	39.4
	22	342	2.96	0.08	500	6960	1240	64.1	12.7	0.66	6620	0.00	27.6
4	0	970	0.00	<0.01	496	22100	1380	104	26.8	2.02	16800	0.00	69.3
	22	469	1.64	0.00	451	2300	1090	71.9	15.4	1.37	9640	0.00	37.0
8	0	1190	6.01	5.62	494	22500	1120	83.4	31.1	1.60	17500	9.86	94.3
	22	207	3.20	3.89	435	6150	551	29.2	6.61	0.00	5050	26.0	20.0
12	0	1610	17.6	11.0	503	37700	916	73.4	34.9	2.76	28900	0.00	139
	22	329	0.59	5.98	417	8620	794	38.2	9.28	1.58	7210	0.00	25.9
19	0	1890	27.6	11.3	487	51700	996	76.6	31.1	5.12	35400	38.7	147
	22	577	15.0	6.55	431	13600	1010	48.6	8.86	0.39	9900	7.35	37.9
27	0	1940	54.0	14.5	428	70000	787	69.9	29.0	3.70	50100	2.02	138
	22	1210	15.0	8.99	445	26500	1230	62.5	16.0	1.18	19100	2.38	66.8

[a], The treatments consisted of a control (zero FGD added) and FGD added at a rate of 22% to the surface (0-15 cm) layer and 5% to the middle (50-65 cm) layer of coal refuse packed into columns (30 x 112 cm).

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